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Modeling and assessment of the $DyCl_3$–KCl system

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Abstract

Experimental thermodynamic data, related to the $DyCl_3$–KCl system and the two pure components have been collected from the literature. Assessment of the collected data has been done using the thermodynamic 'surrounded-ion' model (SIM) and the equations deduced from the thermodynamics of solutions. Gibbs free energy of formation of the two definite compounds K_3DyCl_6 and KDy_3Cl_{10} and the excess entropy of the liquid have been optimized. © 1997 Elsevier Science B.V.

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1. Introduction

The binary system $DyCl_3$–KCl made the object of experimental studies relative to the two pure salts and their mixtures as well.

The phase diagram has already been reported by Korshunov and Drobot [1], Mochinaga et al. [2] and Seifert and Krämer [3]. The equilibrium phase diagram is characterized by two congruently melting definite compounds: K_3DyCl_6 and KDy_3Cl_{10}. Molar enthalpy of mixing of this liquid system has been calorimetrically measured at 1070 K. All the thermodynamic parameters concerning the two pure salts were found from JANAF thermochemical tables [4] for KCl and from Gaune et al. [5,6] for $DyCl_3$.

The goal of this work is to apply the equations deduced from the thermodynamics of solutions for obtaining an analytical form of the excess functions most consistent with the whole set of experimental data.

The 'surrounded-ion' statistical model (SIM) [7,8], has been used in order to describe the behavior of the mixed salts. Indeed, these molten salt mixtures contain ions with different valencies (Dy^{3+}, K^+) and, in general, the thermodynamics of such systems cannot be represented by regular or pseudo-regular models and the ideal entropy differs from that proposed by Temkin [9] for simple melts, e.g. involving ions with the same charge.

The assessment was made in two steps:

- Firstly, we deduced the excess entropy of the liquid by taking into account the liquidus lines relative to the equilibria between the liquid and the solid $DyCl_3$ or the liquid and the solid KCl.
- Secondly, the equilibria between each definite compound and the liquid are considered and the Gibbs free energy of formation of each of them calculated.

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2. Modeling

A lattice description of the $DyCl_3$–KCl melt implies that the substitution to the Dy^{3+} trivalent cation of the K^+ monovalent cation creates two vacancies on the corresponding sublattice. Several relationships have been proposed for the ideal entropy: they differ in the assumptions made on the vacancies. If the number of vacancies is assumed to be negligible, e.g. exchanging a trivalent with a monovalent cation does not induce a localized disordering of the corresponding sublattice, the same result [9] is found for the ideal entropy of mixing. If the number of vacancies is substantial and if no particular association exists between the trivalent ion and the vacancies, Førland [10] found the following relationship for the ideal entropy of mixing:

$$\Delta^{\mathrm{mix}}S = -R[3(1 - x_{\mathrm{K}})\ln(1 - x'_{\mathrm{K}}) + x_{\mathrm{K}}\ln x'_{\mathrm{K}}]$$

where the molar ionic fraction x_{K} and the equivalent ionic fraction x'_{K} are related to the number n_i of i ions:

$$x_{\mathrm{K}} = n_{\mathrm{K}}/(n_{\mathrm{Dy}} + n_{\mathrm{K}})$$

$$x'_{\mathrm{K}} = n_{\mathrm{K}}/(3n_{\mathrm{Dy}} + n_{\mathrm{K}})$$

If the number of vacancies is substantial, and if the divalent ion and the vacancy are assumed to constitute a dimer, Flory [11] proposed for the ideal entropy of mixing

$$\Delta^{\mathrm{mix}}S = -R[(1 - x_{\mathrm{K}})\ln(1 - x'_{\mathrm{K}}) + x_{\mathrm{K}}\ln x'_{\mathrm{K}}]$$

The SIM (see [7,12,13]) provides, from different theoretical grounds, a relationship for the ideal entropy which is identical to the one found by Førland [10].

It should be stressed that many authors do not take into account this charge-dependent expression for the ideal entropy of mixing but arbitrarily use equivalent ionic fractions [10] in the relationships expressing the other functions of mixing and Temkin's ideal entropy. It has been shown [14] that this may lead to some inconsistencies.

The 'surrounded ion' model, already mentioned for melts including ions of the same valency, was extended to asymmetrical mixtures of the kind AX_2-BX_2 [7], AX_2-BX [8], or generally A_pX_q-B_rX_s. For the $DyCl_3$-KCl system, the excess functions, $\Delta^{\mathrm{mix}}H$ for example, are given by:

$$\Delta^{\mathrm{mix}}H = x'(1 - x')(3 - 2x)[\mathrm{P}(x')] \qquad (1)$$

where $\mathrm{P}(x')$ a polynomial with normally the order one.

3. Bibliographical survey

3.1. Pure compounds

All the thermodynamic data relative to KCl ($\Delta^{\mathrm{fus}}H, T^{\mathrm{fus}}, C_p \cdots$) are taken in JANAF thermochemical tables [4]. These values have been used previously in assessment of the $CaCl_2$–KCl system [15]. For $DyCl_3$, temperature and enthalpy of fusion, heat capacity (solid or liquid) at constant pressure, were measured by us in the home laboratory [5,6]. Comparison with data in literature has been done previously [5,6].

KCl
$T^{\mathrm{fus}} = 1044\,\mathrm{K}$; $\Delta^{\mathrm{fus}}H = 26.28\,\mathrm{kJ\,mol^{-1}}$
$C_p(\mathrm{s}) = 40.01 + 0.0255T\,\mathrm{J\,mol^{-1}\,K^{1}}$; $C_p(\mathrm{l}) = 73.60\,\mathrm{J\,mol^{-1}\,K^{-1}}$
$DyCl_3$
$T^{\mathrm{fus}} = 928\,\mathrm{K}$; $\Delta^{\mathrm{fus}}H = 22.80\,\mathrm{kJ\,mol^{-1}}$;
$C_p(\mathrm{s}) = 98.65 + 0.01102T\,\mathrm{J\,mol^{-1}\,K^{-1}}$; $C_p(\mathrm{l}) = 159.43\,\mathrm{J\,mol^{1}\,K^{-1}}$

3.2. Mixtures

3.2.1. Enthalpy of formation

The molar enthalpy of mixing has been measured by Calvet calorimetry by us in the home laboratory [16]. Experimental values were fitted by using the relation (1) in which $\mathrm{P}(x') = a + bx' + cx'^2$. We obtained:

$$a = -23.9 \pm 3.2\,\mathrm{kJ\,mol^{-1}};$$

$$b = -111.2 \pm 14.0\,\mathrm{kJ\,mol^{-1}};$$

$$c = 111.6 \pm 14.5\,\mathrm{kJ\,mol^{-1}}$$

Experimental and calculated data are shown in Fig. 1. Due to the possible formation of ionic complexes in the melt, the last coefficient, c, is needed for taking into account the particular shape of the curve given $\Delta^{\mathrm{mix}}H$, vs. x.

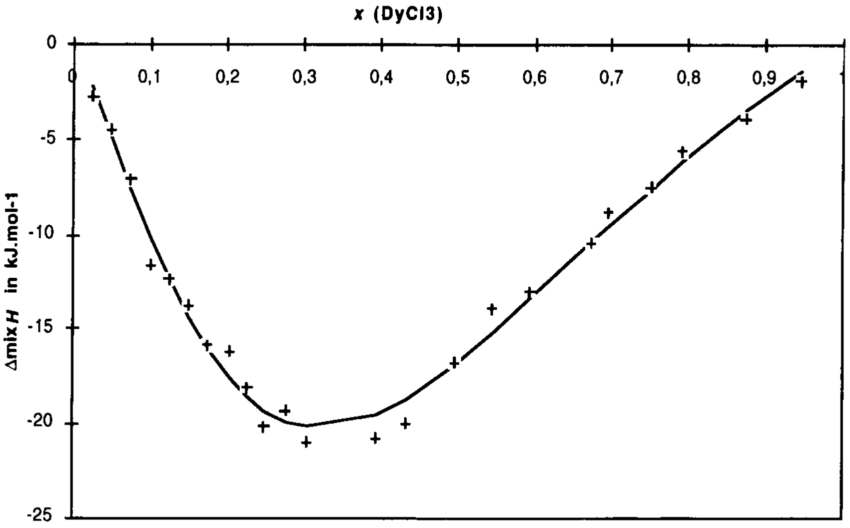

Fig. 1. Excess molar enthalpies, $\Delta^{\mathrm{mix}}H$, for the liquid $DyCl_3$–KCl mixtures against $x(DyCl_3)$: + from Ref. [16]; and ——— calculated from SIM.

3.2.2. *Equilibrium phase diagram*

The equilibrium phase diagram of the $DyCl_3$–KCl system, is characterized by two congruently melting definite compounds (Dy_3KCl_{10}, DyK_3Cl_6) and three eutectic points.

Three authors have investigated this phase diagram. The results presented by Seifert et al. [3], are probably not correct because the melting points of the two pure compounds are very different from the selected values:

$$T^{\mathrm{fus}}(\mathrm{KCl}) = 1073\,\mathrm{K}\,(\mathrm{selected}\;1044\,\mathrm{K});$$
$$T^{\mathrm{fus}}(\mathrm{DyCl_3}) = 919\,\mathrm{K}\,(\mathrm{selected}\;928\,\mathrm{K})$$

The phase diagram proposed by the two other authors are comparable and for the assessment we used the one given by Mochinaga et al. [2].

4. Thermodynamic assessment

The calculation technique is based on the equality of chemical potentials and the minimization of the Gibbs free energy.

The foregoing thermodynamic data were used in conjunction with the 'surrounded-ion' model. This calculation allows optimization of the Gibbs free energy, G, of different phases and their stability as a function of temperature, pressure and composition. The temperature dependence of $G^{\phi}(T) - G^{\mathrm{SER}}(T) = \Delta G$ is given by the following formula:

$$\Delta G = \mathrm{A} + \mathrm{B}T + \mathrm{C}T(1 - \ln T) - \mathrm{D}T^2/2$$

where G^{ϕ}(T) and $G^{\mathrm{SER}}T$ are the Gibbs free energies of the ϕ phase and of the Stable Element Reference, respectively ($G^{\mathrm{SER}}(T) = H(298.15\,\mathrm{K}) - TS(298.15\,))$. For $DyCl_3$ and KCl these coefficients were derived from the above-mentioned values and are presented in Table 1.

The program used in this work is a least squares fitting program for binary systems, simultaneously using the phase diagram and thermodynamic data ($\Delta^{\mathrm{mix}}H$, activities, heat capacities $\cdots$).

The assessment was made in two steps:

- Firstly, we deduced the excess entropy of the liquid by taking into account the liquidus lines relative to the equilibria between the liquid and solid $DyCl_3$ or the liquid and solid KCl.
- Secondly, the equilibria between each solid definite compounds and the liquid are considered and the Gibbs free energy of formation of each of them calculated.

Table 1
Gibbs free energy of $DyCl_3$ and KCl $\Delta G = A + BT + CT(1 - \ln T) - DT^2/2$ (in $J\,mol^{-1}$)

$\Delta(G)$	A	B	C	D
$DyCl_3$(l)	−55326.686	943.5783465	159.43	0
$DyCl_3$(s)	−26467.97	563.0622033	98.65	−0.01102
KCl(l)	−6856.1142	417.2778712	73.6	0
KCl(s)	−11957.883	235.5636696	40.01	−0.0255

5. Results

5.1. Excess entropy

The excess entropy is given by the relation:

$$S^{ex} = (3 - 2x)(1 - x')x'(a + bx' + cx'^2)$$

where a, b, c, were obtained with a correlation coefficient equal to 0.998:

$$a = 42.70 \pm 8.19\,J\,mol^{-1}\,K^{-1}$$

$$b = -130.27 \pm 10.67\,J\,mol^{-1}\,K^{-1}$$

$$c = 73.99 \pm 13.34\,J\,mol^{-1}\,K^{-1}$$

The calculated entropy of mixing, $\Delta^{mix}S = S^{ex} + S^{id}$, is plotted against the composition of the melt in Fig. 2. This entropy is positive in the entire composition range but, as it can be seen, the curve is asymmetrical and in the KCl-rich melts this term is lower. This may be accounted for in terms of the degree of local order. Indeed, in this field of composition the complex anion, $DyCl_6^{3-}$, is probably formed in the melt [16].

5.2. Thermodynamic data of the definite compounds

The Gibbs free energy of formation, $\Delta^{form}G$, of the compounds is referred to the solid state:

$$3DyCl_3(s) + KCl(s) \rightarrow Dy_3KCl_{10}(s);\ DyCl_3(s) + 3KCl(s) \rightarrow DyK_3Cl_6(s)$$

A linear variation of $\Delta^{form}G$ with temperature has been taken into account:

$$\Delta^{form}G = a + bT$$

Results are reported in Table 2.

From $\Delta^{form}G$, it is possible to deduce the enthalpy and the entropy of melting of the compound. The entropy of melting calculated for the DyK_3Cl_6

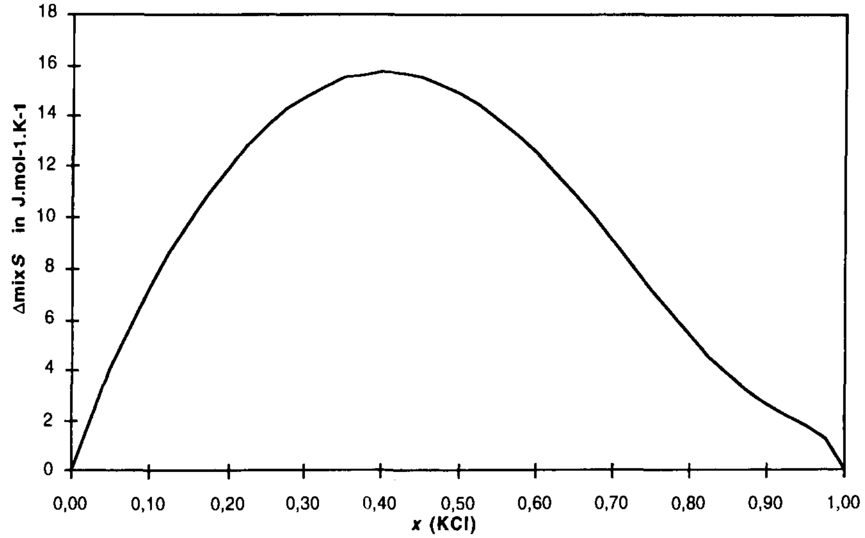

Fig. 2. Molar entropy of mixing of liquid $DyCl_3$–KCl mixtures against x(KCl).

Table 2
Gibbs free energy of formation of the definite compounds $\Delta^{\mathrm{form}}G(\mathrm{s}+\mathrm{s}\rightarrow\mathrm{s}) = \mathrm{a} + \mathrm{b}T$

Compounds	a (kJ mol^{-1})	b (kJ mol^{-1})	Correlation constant
DyK_3Cl_6	−6.67±0.57	−0.0205±0.0006	0.998
Dy_3KCl_{10}	−71.65±4.13	0.0645±0.0051	0.982

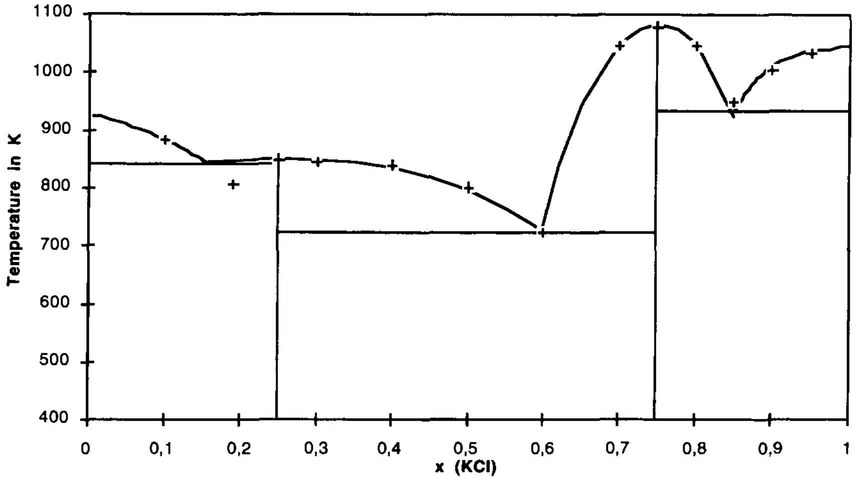

Fig. 3. Phase diagram of the $DyCl_3$–KCl system: + from Ref. [2]; ——— calculated.

compound is equal to: $\Delta^{\mathrm{fus}}S(\mathrm{DyK_3Cl_6}) = 54.62\,J\,mol^{-1}\,K^{-1}$. A comparison with the values of similar compounds given in literature [17] has been made. We obtained: $\Delta^{\mathrm{fus}}S(\mathrm{PrK_3Cl_6}) = 51.8\,J\,mol^{-1}\,K^{-1}$, $\Delta^{\mathrm{fus}}S(\mathrm{NdK_3Cl_6}) = 49.3\,\mathrm{J\,mol^{-1}}$ K^{-1} and $\Delta^{\mathrm{fus}}S(\mathrm{CeK_3Cl_6}) = 43.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$. For this compound the low value indicates that dimers could be formed [17].

For the Dy_3KCl_{10} compound, we obtained: $\Delta^{\mathrm{fus}}H(\mathrm{Dy_3KCl_{10}}) = 92.9\,\mathrm{kJ\,mol^{-1}}$. This value is in good agreement with the one found in literature: $\Delta^{\mathrm{fus}}H(\mathrm{Dy_3KCl_{10}}) = 83.3\,\mathrm{kJ\,mol^{-1}}$ [18].

5.3. Phase diagram

The calculated phase diagram and some experimental points are reported in Fig. 3. Good agreement with the Mochinaga et al.'s experimental results is obtained except for the coordinates of the eutectic located in $DyCl_3$-rich melts:

$$T(\text{calculated}) = 840\,\mathrm{K};\ x(\text{KCl, calculated}) = 0.15,\ \text{instead}\ T = 808\,\mathrm{K}\ \text{and}\ x(\mathrm{KCl}) = 0.19$$

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